



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b> <b>H01L 35/30, H02N 3/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/59047</b> <b>(43) International Publication Date:</b> 5 October 2000 (05.10.00)
<b>(21) International Application Number:</b> PCT/US00/05975 <b>(22) International Filing Date:</b> 6 March 2000 (06.03.00) <b>(30) Priority Data:</b> 60/123,900 11 March 1999 (11.03.99) US <b>(71) Applicant:</b> THERMODYNE TECHNOLOGIES, INC. [US/US]; 391-B Chipeta Way, Salt Lake City, UT 84108 (US). <b>(72) Inventors:</b> KUCHEROV, Yan; 5646 South Park Place East, Salt Lake City, UT 84121 (US). HAGELSTEIN, Peter; Apartment #717, 1500 Worcester Road, Framingham, MA 01702 (US). <b>(74) Agent:</b> EVANS, Paul; Thermodyne Technologies, Inc., 391-B Chipeta Way, Salt Lake City, UT 84108 (US).		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> HYBRID THERMIONIC ENERGY CONVERTER AND METHOD		
<b>(57) Abstract</b>		
<p>The present invention embodies a solid state thermionic energy converter and is directed to a method and apparatus (10, 104, 108) for conversion of thermal energy to electrical energy, and electrical energy to refrigeration. The present invention maintains a thermal separation between an emitter (12) and a collector (16) through a fractional surface contact (13, 42, 44) of decreasing cross-sectional area towards the point of contact. The fractional surface contacts (13, 42, 44) may be associated with the emitter (12), a barrier (14), or the collector (16). Maintaining a thermal separation between the emitter (12) and the collector (16) provides for ballistic electron transport through the barrier (14) and reduces the transport of electrons through thermal conductivity. Hence, the efficiency is increased through the collection of ballistic electrons and the reduction of thermal conductivity electrons which cannot be collected. The inventive principle works for hole conductivity, as well as for electrons.</p> <div data-bbox="602 1136 1349 1482" data-label="Diagram"> </div>		
<b>BEST AVAILABLE COPY</b>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## HYBRID THERMIONIC ENERGY CONVERTER AND METHOD

### FIELD OF THE INVENTION

This invention relates to the conversion of thermal energy to electrical energy, and electrical energy to refrigeration, and more particularly to a thermionic converter of improved efficiency and power densities, which utilizes electron tunneling and thermionic emission facilitated by the reduction in the barrier height from image force effects:

### BACKGROUND OF THE INVENTION

The present invention was developed to fill a need for a device which efficiently converts thermal energy to electrical energy at relatively low operating temperatures and with power densities large enough for commercial applications. The present invention also operates in reverse mode to provide efficient cooling.

Thermionic energy conversion is a method of converting heat energy directly into electrical energy by thermionic emission. In this process, electrons are thermionically emitted from the surface of a metal by heating the metal and imparting sufficient energy to a portion of the electrons to overcome retarding forces at the surface of the metal in order to escape. Unlike most other conventional methods of generating electrical energy, thermionic conversion does not require either an intermediate form of energy or a working fluid, other than electrical charges, in order to change heat into electricity.

In its most elementary form, a conventional thermionic energy converter consists of one electrode connected to a heat source, a second electrode connected to a heat sink and separated from the first electrode by an intervening space, leads connecting the electrodes to the electrical load, and an enclosure. The space in the enclosure is either highly evacuated or filled with a suitable rarefied vapor, such as cesium.

The essential process in a conventional thermionic converter is as follows. The heat source supplies heat at a sufficiently high temperature to one electrode, the emitter, from which electrons are thermionically evaporated into the evacuated or

rarefied-vapor-filled interelectrode space. The electrons move through this space toward the other electrode, the collector, which is kept at a low temperature near that of the heat sink. There the electrons condense and return to the hot electrode via the electrical leads and the electrical load connected between the emitter and the collector.

5           The flow of electrons through the electrical load is sustained by the temperature difference between the electrodes. Thus, electrical work is delivered to the load.

          Thermionic energy conversion is based on the concept that a low electron work function cathode in contact with a heat source will emit electrons. These  
10       electrons are absorbed by a cold, high work function anode, and they can flow back to the cathode through an external load where they perform useful work. Practical thermionic generators are limited by the work function of available metals or other materials that are used for the cathodes. Another important limitation is the *space charge effect*. The presence of charged electrons in the space between the cathode and  
15       anode will create an extra potential barrier which reduces the thermionic current.

          Typical conventional thermionic emitters are operated at temperatures ranging from 1400 to 2200K and collectors at temperatures ranging from 500 to 1200K. Under optimum conditions of operation, overall efficiencies of energy conversion range from 5 to 40%, electrical power densities are of the order of 1 to 100 watts/cm<sup>2</sup>,  
20       and current densities are of the order of 5 to 100 A/cm<sup>2</sup>. In general, the higher the emitter temperature, the higher the efficiency and the power and current densities with designs accounting for radiation losses. The voltage at which the power is delivered from one unit of a typical converter is 0.3 to 1.2 volts, i.e., about the same as that of an ordinary electrolytic cell. Thermionic systems with a high power rating frequently  
25       consist of many thermionic converter units connected electrically in series. Each thermionic converter unit is typically rated at 10 to 500 watts.

          The high-temperature attributes of thermionic converters are advantageous for certain applications, but they are restrictive for others because the required emitter temperatures are generally beyond the practical capability of many conventional heat  
30       sources. In contrast, typical thermoelectric converters are operable at heat source temperatures ranging from 500 to 1500K. However, even under optimum conditions,

overall efficiencies of thermoelectric energy converters only range from 3 to 10%, electrical power densities are normally less than a few watts/cm<sup>2</sup>, and current densities are of the order of 1 to 100 A/cm<sup>2</sup>.

From a physics standpoint, thermoelectric devices are similar to thermionic devices. In both cases a temperature gradient is placed upon a metal or semiconductor, and both cases are based upon the concept that electron motion is electricity. However, the electron motion also carries energy. A forced current transports energy for both thermionic and thermoelectric devices. The main difference between thermoelectric and thermionic devices is whether the current flow is diffusive (thermoelectric) or ballistic (thermionic). A thermionic device has a relatively high efficiency if the electrons ballistically go over and across the barrier. For a thermionic device all of the kinetic energy is carried from one electrode to the other. The motion of electrons in a thermoelectric device is quasi-equilibrium and diffusive, and can be described in terms of a Seebeck coefficient, which is an equilibrium parameter.

In structures with narrow barriers, the electrons will not travel far enough to suffer collisions as they cross the barrier. Under these circumstances, the thermionic emission theory is a more accurate representation of the current transport. The current density is given by:

$$j = A_0 T^2 e^{\frac{-e\varphi}{kT}}, \text{ where } A_0 \text{ is the Richardson's constant, } \varphi \text{ is the barrier height}$$

(electron work function),  $e$  is the electron charge,  $k$  is Boltzmann's constant, and  $T$  is the temperature. Richardson's constant  $A_0$  is given by  $A_0 = (em\kappa^2 T^2)/(2\pi^2 \hbar^2)$ , where  $m$  is the effective electron mass and  $\hbar$  is Plank's constant.

The diffusion theory is appropriate for barriers in which the barrier thickness (length) is greater than the electron mean-free-path in one dimension, while the thermionic emission theory is appropriate for barriers for which the barrier thickness (length) is less than the mean-free-path. However, if the barrier becomes very narrow, current transport by quantum-mechanical tunneling becomes more prominent.

There remains a need to provide a more satisfactory solution to converting thermal energy to electrical energy at lower temperature regimes with high efficiencies and high power densities.

5

### SUMMARY OF THE INVENTION

The present invention seeks to resolve a number of the problems which have been experienced in the background art, as identified above. More specifically, the apparatus and method of this invention constitute an important advance in the art of thermionic power conversion, as evidenced by the following objects and advantages realized by the invention over the background art.

10

An object of the present invention is to generate high power densities and efficiencies of a typical thermionic converter, but to operate at temperature regimes of typical thermoelectric devices.

15

Another object of the present invention is to maintain thermal separation between the emitter and collector.

A further object of the present invention is to minimize the effects of thermal expansion.

Additional objects and advantages of the invention will be apparent from the description which follows, or may be learned by the practice of the invention.

20

Briefly summarized, the foregoing and other objects are achieved by an apparatus which comprises: an electrically and thermally conductive electron emitter; an electrically and thermally conductive electron collector for receiving electrons from the emitter; a solid-state barrier disposed between and in intimate contact with said emitter and collector for filtering high energy electrons transferred from the emitter to the collector; one or more electrically and thermally conductive fractional surface contacts disposed between and in intimate contact with the emitter and barrier, or the barrier and collector, or a combination thereof; a thermally and electrically nonconductive space adjacent to the fractional surface contacts and the emitter and barrier, or the barrier and collector, or a combination thereof; and an electric load connected to the emitter and collector.

25  
30

In the refrigeration embodiment, carrier transport is assisted by a potential applied between the emitter and collector, and the emitter is connected to a thermal load that is cooled by heat flow to the emitter. A heat exchanger dissipates the heat from hot electrons on the collector.

5

### BRIEF DESCRIPTION OF DRAWINGS

In order to more fully understand the manner in which the above-recited advantages and objects of the invention are obtained, a more particular description of the invention will be rendered by reference to specific embodiments thereof which are illustrated in the appended drawings. Understanding that these drawings depict only typical embodiments of the invention and are therefore not to be considered limiting of its scope, the presently preferred embodiments and the presently understood best mode of the invention will be described with additional detail through use of the accompanying drawings in which:

10

15

FIG. 1 is a cross-sectional view of a thermionic converter of the present invention.

FIG. 2 illustrates a cross-sectional view of a fractional surface contact having a triangular cross-section.

20

FIG. 3 shows a perspective view of an emitter utilizing tantalum-hydride powder with a honeycomb structure to support the powder.

FIGS. 4A and 4B shows a cross-sectional view of a low thermal conductivity semiconductor barrier placed in a vacuum between a metal emitter and a metal collector.

25

FIG. 5 illustrates a plot of Richardson thermionic current density versus barrier height at various temperatures.

FIG. 6 illustrates the thermal expansion pattern and nanowire positioning for a circular plate.

FIG. 7 illustrates the thermal expansion pattern and nanowire positioning for a rectangular plate.

30

FIG. 8 illustrates various nanowire cross-sections.

FIG. 9 is a cross-sectional view of an embodiment of the present invention wherein the fractional surface contact is associated with the barrier.

FIG. 10 is a cross-sectional view of a barrier configuration comprising a metallic layer, an n-type semiconductor layer, a p-type semiconductor layer, and a metallic layer.

FIG. 11 is a cross-sectional view of a barrier configuration comprising a metallic layer, an n-type semiconductor layer, and a metallic layer.

FIG. 12 is a cross-sectional view of a barrier configuration comprising a metallic layer, a p-type semiconductor layer, and a metallic layer.

FIG. 13 is a cross-sectional view of a barrier configuration comprising a resonant tunneling diode.

FIG. 14 shows the transmission probability for a specific GaAs-Al<sub>x</sub>Ga<sub>1-x</sub>As heterostructure.

FIG. 15A shows a cross-sectional view of a nonmetallic collector with a metallic layer.

FIG. 15B shows a cross-sectional view of a nonmetallic collector with a metallic layer and a surface barrier matching material disposed between the collector and the barrier to prevent the leak back of electrons to the emitter.

FIG. 16 is an I-V curve for an emitter comprising TaH and a barrier comprising Al<sub>2</sub>O<sub>3</sub>.

FIG. 17 is an I-V curve for an emitter comprising TaH and a barrier comprising Al<sub>2</sub>O<sub>3</sub> at a different temperature differential than FIG. 16.

FIG. 18 is a plot of the voltage dependence on the temperature gradient for an emitter comprising TaH and a barrier comprising Al<sub>2</sub>O<sub>3</sub>.

FIG. 19 is an I-V curve for an emitter comprising TiH<sub>2</sub>, a barrier comprising PbTe, and a collector comprising Pt on an Al substrate.

FIG. 20 shows a cross-sectional view of a thermionic converter for providing refrigeration.

FIG. 21 shows a cross-sectional view of a barrier in the form of point contacts (microspheres) in a refrigeration embodiment.

FIG. 22 shows cross-sectional view of a barrier in the form of microspheres comprising a non-thermally conductive core material having an outer metallic layer and a semiconductor layer.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention embodies a thermionic energy converter 10 and is directed to a method and apparatus for conversion of energy generally illustrated in Figure 1. The present invention 10 comprises an electrically and thermally conductive electron emitter 12, an electrically and thermally conductive electron collector 16 for receiving electrons from the emitter 12, a solid-state barrier 14 disposed between and in intimate contact with said emitter 12 and collector 16 for filtering high energy electrons transferred from the emitter 12 to the collector 16, and an electric load connected to said emitter 12 and collector 16.

The present invention 10 maintains a thermal separation between the emitter 12 and the collector 16 through a fractional surface contact 13, such as that shown in Figure 1. Maintaining a thermal separation between the emitter 12 and the collector 16 provides for ballistic electron transport through barrier 14 and reduces the transport of phonons and electrons through thermal conductivity. Hence, the efficiency is increased through the collection of ballistic electrons and the reduction of thermal conductivity electrons which cannot be collected. It is also important to note that the inventive principle works for hole conductivity, as well as for electrons. Also, reference to metals herein includes alloys.

The fractional surface contact 13 is defined by a fractional surface geometry of decreasing cross-sectional area towards fractional surface contact 13. For example, Figure 1 illustrates a fractional surface contact 13 which is defined by a barrier 14 comprised of spherical particles, wherein the fractional surface geometry is a spherical shape. The fractional surface contacts may be integral to the emitter 12, the barrier 14, or the collector 16. The emitter 12, barrier 14, or collector 16 has one or more fractional surface contacts 13 disposed between and in intimate contact with the emitter 12 and barrier 14, or the barrier 14 and collector 16, or a combination thereof.

The fractional surface contact 13 also provides for quantum mechanical tunneling, for example, along the non-contacting surface of the fractional contact 13 and between the collector 16 at a distance of  $50\text{\AA}$  or less. This distance depends upon the materials utilized and their corresponding work functions. The fractional surface contact 13 also provides for thermionic emission facilitated by the reduction in the barrier height from image force effects, for example, along non-contacting surface of the fractional contact 13 and between the collector 16 at a distance of  $25\text{\AA}$  or less. This distance also depends upon the materials utilized and their corresponding work functions. See Coutts, T.J. *Electrical Conduction in Thin Metal Films*. N.Y., Elsevier Scientific Publishing Co., 1974, pp. 54-55, for a discussion of the image force effect.

Figure 2 illustrates a fractional surface contact 13 having a triangular cross-section that acts as point emitters or contacts. Other examples of various fractional surface contact shapes include, but are not limited to, parabolic-shaped contacts, elliptical-shaped contacts, curved-shaped contacts, nanotubes, particles, dendrites made from methods such as micro-lithography and holographic lithography, Tonks' method (electric instability on liquid metal surface), ion milling, or equivalents thereof.

A thermally and electrically nonconductive space 15, including but not limited to a vacuum, xenon, radon, or other nonconductive gas, is adjacent to the fractional surface contacts 13 and the emitter 12 and barrier 14, or the barrier 14 and collector 16, or a combination thereof. Space 15 reduces electrons that would otherwise be thermally transported and assists in maintaining a thermal separation between the emitter 12 and the collector 16.

Electron flow occurs when an electrical load  $R_L$  is connected to the emitter 12 and collector 16, where the work function of the emitter 12 is less than the work function of the collector 16. When determining the load resistance, it is noted that the maximum efficiency for any electric power source normally occurs when the internal resistance of the power source is the same as the load resistance. Therefore, if the internal resistance is very low, the desired load resistance should also be very low.

If the barrier 14 is adjusted to sort hot electrons, the emitter 12 will be cooled and the electron current will result in the potential increase on the collector 16. To achieve a desirable converter efficiency, the barrier 14 must effectively stop electrons with lower energies. The emitter 12 and the barrier 14 are matched such that electron concentration on the emitter 12 is higher than electron concentration on the collector 16 at a given energy defined by the barrier height.

Utilizing materials with a low reflectance on the emitter side and a high reflectance on the collector side are beneficial for maintaining a high efficiency.

## 1. Emitter

The emitter 12 comprises an electrically and thermally conductive material, such as metals, metal alloys, semiconductor or doped semiconductor materials. The emitter 12 may also comprise an electrically and thermally conductive layer on a substrate, such as materials including, but not limited to,  $\text{SiO}_2$ , glass, quartz, or equivalents thereof, coated with a metallic layer or other thermally and electrically conductive material.

Another embodiment of the present invention wherein the fractional surface contact is associated with the emitter utilizes a high phonon energy material as the emitter 12, preferably with a mean energy of at least about  $3 kT$ , to distort the electron energy distribution using electron-phonon interaction. Materials exhibiting these characteristics are metal hydrides  $\text{Me}_x\text{H}_y$ , irrespective of stoichiometry. Examples include, but are not limited to,  $\text{TiH}_x$ ,  $\text{VH}_x$ ,  $\text{ZrH}_x$ ,  $\text{NbH}_x$ ,  $\text{TaH}_x$ ,  $\text{ScH}_x$ ,  $\text{YH}_x$ ,  $\text{ThH}_x$ ,  $\text{UH}_x$ , all rare earth hydrides, or combinations thereof. Many metals which form hydrides may be alloyed with normal metals even to high concentrations without losing the high energy component in their phonon spectrum and may have better properties in terms of oxidation, e.g.,  $\text{TaCu}$  or  $\text{TiCu}$  alloys. The emitter 12 should also provide thermal and electrical conductivity.

Figure 3 illustrates an example of an emitter comprising a metal hydride powder 17 supported in a honeycomb structure 18.

In general, all metal hydrides  $\text{Me}_x\text{H}_y$  have median phonon energy in their spectra of more than 100 meV, with the exception of Pd and Pd alloys.  $\text{Me}_x\text{H}_y$  is

preferable over  $\text{Me}_x\text{D}_y$  (or  $\text{Me}_x\text{T}_y$ ), since the  $^1\text{H}$  isotope is lighter and provides higher phonon frequencies (energies). It should also be noted that the phonon frequency is basically independent of the hydrogen concentration (See Landolt-Börnstein, *Numerical Data and Functional Relationships in Science and Technology, Group III: Crystal and Solid State Physics*, (1983) Vol. 13b *Metals: Phonon States, Electron States and Fermi Surfaces*, pp. 333-354, the contents of which are specifically incorporated herein.).

Other stable materials with high phonon energies include, but are not limited to, BH,  $\text{B}_4\text{C}$ , BN (hexagonal), BN (cubic), diamond, or combinations thereof. An emitter 12 using a non-conductive substrate must also have a conductive or doped layer, such as silver, with a thickness less than the electron mean free path, in order to emit electrons into the barrier 14. Alternatively, the conductive or doped layer may be placed on the barrier 14 when the emitter 12 comprises a thermally and electrically non-conductive material. A conductive or doped layer provides thermal and electrical conductivity. For example, if the emitter 12 comprises BN microspheres and the conductive or doped layer comprises Ag (electron mean free path is  $400\text{\AA}$ ), the conductive or doped layer thickness is preferably between  $50\text{-}200\text{\AA}$ .

## 2. Barrier

Most semiconductors with a low forbidden gap have a very low thermal conductivity, such as a few  $\text{W}/(\text{m}\cdot\text{K})$ , or roughly 100 times less than for copper or silver. This provides for a barrier geometry selection corresponding to at least a few degrees of thermal separation between the emitter 12 and the collector 16. This embodiment is illustrated in Figures 4A and 4B, wherein a low thermal conductivity semiconductor barrier 14 (e.g., fixed pillars, microspheres, etc.) is placed in a vacuum between a metal emitter 12 and a metal collector 16. The emitter 12 is at a higher temperature than the collector 16. Isotherms (different scale in two materials) are indicated by dashed lines 19. The spacing of isotherms 19 is much larger in metals due to a larger thermal conductivity. Estimations for a thermal conductivity difference of 100:1 result in a bridge cross-sectional linear dimension (e.g., diameter) of up to one micron. Area A will then emit electrons, since it is facing a low barrier on a

metal-semiconductor interface (a fraction of 1eV). Area B will not emit electrons, since it is facing a metal-vacuum interface with a few eV potential barrier. The ratio of area A to area B will define the decrease in the thermal conductivity of the gap (without a radiation component). For example, a 1:100 ratio provides for a thermal separation of 100K between the emitter 12 and collector 16. Decreasing the emitter 12 area by 100 times will require relatively high current densities. A graph of the Richardson current density as a function of the barrier height and temperature is shown in Figure 5. Line 20 represents values at 300K; line 22 represents values at 350K; line 24 represents values at 400K; line 26 represents values at 500K; line 28 represents values at 700K; line 30 represents values at 800K; and line 32 represents values at 900K. For instance, a 1W device having a total area of 1cm<sup>2</sup> and a temperature of 400K on the emitter 12, will require a Richardson current of approximately 10<sup>3</sup>A/cm<sup>2</sup>. This current can be achieved with a barrier of 0.35eV, such as PbTe. 10<sup>4</sup>-10<sup>5</sup>A/cm<sup>2</sup> is an electromigration practical limit for doped semiconductors with a small forbidden gap.

The embodiments illustrated in Figures 4A and 4B can be constructed with known techniques such as micro-lithography or holographic lithography. However, thermal expansion characteristics must be considered for certain materials. For example, a 1cm<sup>2</sup> metal plate end with a thermal expansion coefficient of 10<sup>-5</sup>K<sup>-1</sup> will travel 10<sup>5</sup>Å at a 100K temperature change, which is inconsistent with a bridge length of only a few hundred angstroms. Therefore, the barrier 14 preferably should be a moveable (rolling or sliding) barrier. A moveable barrier 14 may comprise microspheres or short microwires disposed between an emitter 12 and a collector 16. Microspheres are preferable because of an absence of thermal expansion and orientation challenges. The microsphere embodiment is illustrated in Figure 1, wherein 5-100 nanometer-size semiconductor spheres 14 are available from precipitation, aerosol, or plasma spray manufacturing methods. However, advances in submicron lithography make the nanowire approach feasible from a technological point of view. The nanowire approach requires uniform and stress-relieved materials on both the emitter 12 and collector 16 sides. The simplest design is a circular plate which expands radially. Figure 6 illustrates the expansion pattern 34 and nanowire

positioning 36 of a circular plate. It should be noted that plate movement across the nanowire may cause degradation after a few thermal cycles, and should be avoided. A rectangular plate provides a more complex thermal expansion pattern 38, as illustrated in Figure 7. Figure 7 shows that nanowire positioning 40 is relatively complex and will be effective when the absolute size change is relatively small to avoid second order effects. The plate preferably should have a small thermal expansion coefficient to minimize the absolute size change at elevated temperatures.

Circular and rectangular emitter 12 and collector 16 plate geometries are not the only possible configurations. However, each configuration has its own thermal expansion pattern, which must be analyzed mathematically with the nanowire orientation designed accordingly. A nanowire cross-section can vary depending upon the materials used, operating temperatures, and temperature gradients. Some example cross-sections 42 include, but are not limited to, those illustrated in Figure 8.

The potential barrier for electrons with this embodiment can be formed only with Schottky barriers. Examples of known Schottky barriers for some of the semiconductors in contact with metals are shown in Table 1 below. This list can be expanded for basically any Schottky barrier, or when comparing an interface material's electron work function with the vacuum energy level (See *Band Structure Engineering in Semiconductor Microstructures*, NATO ASI Series, Series B: Physics, Vol. 189 (1988), p. 24. Lerach, L. and Albrecht, H. *Current Transport in Forward Biased Schottky Barriers on Low Doped n-Type InSb*, North-Holland Publishing Co., 1978. pp. 531-544.; Brillson, L. *Contacts to Semiconductors, Fundamentals and Technology*, Noyes Publications, 1993; Rhoderick, E. H. and Williams R. H. *Metal-Semiconductor Contacts*, Second Edition, Clarendon Press, 1988.). Positioning of the spheres 14 may be made by precipitation from a liquid, dielectrophoresis, vibration/charge, masking or equivalents thereof. For example, dielectrophoresis involves a powder assuming a charge in a dielectric medium, such as ethyl alcohol. It is important to use fresh ethyl alcohol, since the alcohol will pick up water from the atmosphere. This will make the medium somewhat conductive and the process will degrade. The charge moves when an electric field is applied. The controls for coating

are the voltage applied and the concentration of powder in the mixture. The powder is dispersed by ultra sonics or shaking.

5 As set forth previously, if the emitter 12 comprises a non-metallic material, a metallic layer may be placed on either the emitter 12 or the barrier 14. For example, the barrier 14 comprising microspheres illustrated in Figure 1 would include an outer metallic layer and metal contacts placed on the emitter 12.

TABLE 1

Material	Barrier (eV)
Si	0.5-0.8
n-Ge	0.18-0.45
n-GaAs	0.70
n-InAs	0.50
n-GaSb	0.07
n-InSb	~0.1
Sb	~0.1
n-PbS	~0.2
n-PbSe	~0.2
p-Cu <sub>2</sub> O	0.4
p-Se	0.30-0.55
n-CDs	0.88
DySi <sub>2</sub>	0.37
IrSi <sub>3</sub>	0.94
Hg <sub>x</sub> Cd <sub>1-x</sub> Te	0.0-0.5
p-Ge	0.26
B (Amorphous)	0.43
LaB <sub>6</sub>	0.35
YbB <sub>6</sub>	0.30
Pd <sub>2</sub> Si	0.7
n-PbTe	0.32
p-GaAs	0.55
n-InP	0.32-0.54

Table 1 shows various materials having a barrier height in the range of 0.1eV to 1.0eV. All practical temperatures are included in Figure 5 for the materials listed in Table 1. For example, n-GaAs or Pd<sub>2</sub>Si (0.7eV) are acceptable barrier materials at an

operation temperature of 800K, 1:100 area coverage, and  $10^3 \text{ A/cm}^2$  current limit through the barrier material ( $\approx 1 \text{ W/cm}^2$  converter specific power). Semiconductors may also be doped with impurities that provide for sub-band conduction. For example, doping Ge with Te provides a donor sub-bandwidth of 0.3eV spacing from the conductance band bottom, thus changing the intrinsic surface barrier by a value of 0.15-0.20eV.

An example of the embodiment illustrated in Figure 1 may comprise semiconductor spheres with a  $100\text{\AA}$  diameter deposited on a variety of substrates with a desired density per unit area by methods such as laser ablation, or equivalents thereof. The surface finish on semiconductors and dielectrics is preferably within a few angstroms RMS; however, the surface must be metallized. Metal coatings with a  $10\text{\AA}$  RMS surface are routine with magnetron sputtering. Standard optical polishing provides 1-3 arcmin. parallelism. Without a flexible plate on one side, the absence of electrical shorts can only be guaranteed over a distance of about 100 microns. Materials having a thickness of approximately 0.1 mm or less such as glass, quartz, Si, Ge, mica, or equivalents thereof, will function as a local spring and compensate for parallelism if a thermally conductive cushion such as carbon fibers, or equivalents thereof, are used as an intermediate layer for compression.

To illustrate thermal management and compression challenges, the embodiment shown in Figure 9 comprises  $100\text{\AA}$  germanium spheres 44 between two ideally smooth molybdenum 46 or molybdenum coated plates 48 of  $1 \times 1 \text{ cm}^2$  squares, with a 100K temperature difference between plates 46 and 48 and a 10W heat flow across the converter. One of the plates 46 or 48 is thin enough (e.g., 10-20 microns) to be sufficiently flexible to compensate locally for parallelism problems.

The heat flow  $q$  is supplied by a heat source (not shown). A thermal differential is maintained between the cold plate 46 at a temperature  $T_2$  and a hot plate 48 at a temperature  $T_1$ . In this case,  $T_1 - T_2 = 100\text{K}$ . Plate 48 is made of a silicon wafer material having a thickness of 10 microns and metallized with a  $2000\text{\AA}$  molybdenum coating on both sides. Ge nanospheres 44 are deposited by laser ablation onto plate 46. A thin layer of carbon fibers 50 provide for a uniform load on the plate 48 and conduct heat and electrical flow through the flat compressing plate

52. The mechanical load on the nanospheres 44 is regulated by calibrated springs 54. In principle, the springs 54 may also be attached to plate 46 instead of plate 52. The compression force supplied by springs 54 defines the deformation of the spheres 44, and indirectly defines the thermal and electric contact properties on the sphere-plate interface. The entire device is enclosed in a vacuum chamber and evacuated to a residual pressure below  $5 \times 10^{-4}$  torr. At this pressure the thermal conductivity of air is smaller than the radiative losses at room temperature (see Kaganer, M.G. *Thermal Insulation in Cryogenic Engineering*. Israel Program for Scientific Translations Ltd. 1969. Pp7-106.). Kaganer discusses that the thermal resistance on the interface is a complex function of many parameters. For simplicity, the following example assumes that the thermal resistance of the sphere 44 is equivalent to a rod having a cross-section of  $1000 \text{ \AA}^2$ . The specific heat flow ( $q_1 = \kappa \partial T / \partial y$ ) through one contact with a thermal conductivity,  $\kappa$ , value of  $40 \text{ W/(mK)}$  for germanium, yields a value of  $4 \times 10^{-6} \text{ W}$ . To maintain a 100K temperature gradient at 10W total heat flow requires  $2.5 \times 10^6$  spheres, or approximately 6 micron spacing between the spheres 44, which corresponds to about 3 arcminutes of plate parallelism that is standard for thin silicon wafers.

It can be assumed that under compression the Ge sphere 44 will deform and the plate 46 will remain flat since the elasticity modulus for Mo (300 GPa) is much higher than for Ge (82 GPa). The calculations show that approximately a  $10^{-7} \text{ N}$  force is required to provide  $1000 \text{ \AA}$  contact area. The total compressive force in this case will be 0.25N, which is relatively small and allows for only a partial plate parallelism compensation with a 10 micron thick silicon plate. Improved results are possible with thinner plates or a more flexible plate material such as glass.

The previous example also illustrates the optimization principle for this device. If the desired temperature differential is increased to 200K, 20 watts of heat flow must be supplied to the device. If only 10 watts are available, the number of nanospheres must be cut by two, and so forth.

Examples of various barrier 14 materials are disclosed in the following references, the contents of which are specifically incorporated herein: Burstein, E. and Lundqvist, S. *Tunneling Phenomena in Solids*. N.Y., Plenum Press, 1969. pp. 47-78,

127-134, 149-166, and 193-205. Mizuta, H. and Tanoue, T. *The Physics and Applications of Resonant Tunneling Diodes*. N.Y. Cambridge University Press, 1995. pp. 52-87. Duke, C.B. *Tunneling in Solids*. N.Y., Academic Press 1969. pp. 49-158, and 279-290. Conley, J. W. and Tiemann, J.J. *Experimental Aspects of Tunneling in Metal-Semiconductor Barriers*. *Journal of Applied Physics*, Vol. 38, no. 7 (June 1967), pp. 2880-2884. Steinrisser, F. and Davis, L.C. *Electron and Phonon Tunneling Spectroscopy in Metal-Germanium Contacts*. *Physical Review*, Vol. 176, no. 3 (December 15, 1968), pp. 912-914. Hicks, L.D. and Dresselhaus, M.S. *Effect of Quantum-well Structures on the Thermoelectric Figure of Merit*. *Physical Review B*, Vol. 47, no. 19 (May 15, 1993), pp. 12 272-12 731. Abram, R.A. and Jaros, M. *Band Structure Engineering in Semiconductor Microstructures. Series B: Physics*, Vol. 189, N.Y. Plenum Press 1988. pp. 1-6, and 21-31. Ferry et al. *Quantum Transport in Ultrasmall Devices. Series B: Physics*, Vol. 342, N.Y. Plenum Press 1995. pp. 191-200. Shakorui, A. and Bowers, J.E. *Heterostructure Integrated Thermionic Coolers*. *Applied Physics Letters*, Vol. 71, no. 9 (September 1, 1997), pp. 1234-1236.

One skilled in the art of applying thin barrier materials recognizes the need for cleanliness and to avoid contamination such as bacteria, foreign particles, dust, etc. It is also important to prepare a smooth surface finish on the substrate on which the barrier is placed.

Dielectrics in the pure form have extremely high barrier properties. For example, a typical forbidden gap for a dielectric is 4-6 eV. It is extremely difficult to thermally excite electrons to this kind of energy, in order to provide a significant current. Impurities and lattice defects within dielectrics provide local conductive bands that give lower barriers.

The behavior of lattice defects and impurities in dielectrics has not been extensively explored, see e.g., Hill, R.M. *Single Carrier Transport in Thin Dielectric Films*. Amsterdam, Elsevier Publishing Co., 1967. pp. 39-68, the contents of which are specifically incorporated herein. In principle, the barrier height may be controlled by changing the impurity type and concentration. Conduction by multi-step tunneling through defects also provides some conductivity at a low electron energy.

One skilled in the relevant art recognizes there are a variety of deposition techniques that may be employed to form ultra thin dielectric coatings, which include, but are not limited to, CVD (chemical vapor deposition), PVD (physical vapor deposition), in their various forms such as magnetron, electron beam, pulsed laser deposition, or equivalents thereof. These deposition techniques are known for the deposition of 10-500Å layers of dielectrics, such as Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>.

The electron energy sorting barrier 14 may also utilize semiconductors, rather than dielectrics. Since the metal-semiconductor interface barrier can be selected for a desired barrier height value, a metal-semiconductor potential barrier can be more easily regulated than a metal-dielectric-metal junction. A metal-semiconductor junction exhibits tunneling properties for highly degenerated semiconductors, for example heavily doped semiconductors, which allows for thin potential barriers.

Three types of semiconductor barriers can be used: (1) conductive or doped material 62/n-type semiconductor 64/p-type semiconductor 66/conductive or doped material 68 (see Figure 10; note also that the n-type and p-type layers may be reversed); (2) conductive or doped material 70/n-type semiconductor 72/conductive or doped material 74 (see Figure 11); and (3) conductive or doped material 76/p-type semiconductor 78/conductive or doped material 80 (see Figure 12). In this embodiment, an electron injected into a p-type region can be accelerated by a local electric field. Examples of semiconductor materials are disclosed in the following references, the contents of which are specifically incorporated herein. See Landolt-Börnstein, *Numerical Data and Functional Relationships in Science and Technology, Group III: Crystal and Solid State Physics*, (1982) Vols. 17b-17i and (1987) Vol. 22a *Semiconductors*. Madelung, O. *Data in Science and Technology. Semiconductors Other than Group IV Elements and III-V Compounds*. N.Y., Springer-Verlag Berlin Heidelberg, 1992. pp. 1-153. Conwell, E. M., *Semiconductors I*, Bulletin of American Physical Society, Vol. 10, (June 14, 1965), p. 593. Hall R. N. and Racette J. H. *Band Structure Parameters Deduced from Tunneling Experiments*, Journal of Applied Physics, Supp. to Vol. 32, no. 10 (October 1961), pp. 2078-2081.

With a forbidden gap energy  $E_g$ , the first barrier will have an exponential factor  $E_g$  and a second exponential factor of approximately  $E_g/2$  (without a Schottky barrier associated with surface defects and crystallography).

Barrier heights for semiconductors are lower than corresponding barriers for dielectrics. The barrier 14 thickness is not as crucial with a semiconductor and the barrier height can be adjusted using a proper semiconductor material. For example, the semiconductor thickness may be in the region of hundreds of angstroms (or thicker) compared to tens of angstroms required for a dielectric. A thicker barrier 14 is much easier to manufacture because it is less susceptible to pin holes, dust and other contaminants. Also, the current exponentially depends on the barrier height.

From Richardson's Equation with a semiconductor having a barrier height  $\phi$  equal to 150 meV, the current density at room temperature is very high, roughly  $\geq 10^6$  A/cm<sup>2</sup> and  $\sim 10^4$  A/cm<sup>2</sup> at  $\phi$  equal to about 300 meV. Semiconductors having a barrier height of less than 0.6 to 0.7eV may be used in this embodiment, since reasonably high current densities ( $>1$  A/cm<sup>2</sup>) may be provided.

A resonant tunneling (RT) barrier 81 comprises two or more barriers 82 and 86 with a spacing 84 between barriers 82 and 86 that is sufficient for electrons to form a standing wave (see Figure 13). Spacing 84 is typically 100Å or less and requires a precision deposition technique, such as molecular beam epitaxy (MBE), or equivalents thereof. The physics and technology of RT devices is disclosed in Mizuta, H. and Tanoue, T. *The Physics and Applications of Resonant Tunneling Diodes*. Cambridge University Press, 1995. pp. 1-235, the contents of which are specifically incorporated herein.

The advantage of a resonant tunneling barrier 81 is in its selective electron energy dependent transmission. The example of the transmission probability for a specific GaAs-Al<sub>x</sub>Ga<sub>1-x</sub>As heterostructure is given in Figure 14. From Figure 14 it can be seen that there are a few transmission peaks, each one of which is a multiple of the fundamental harmonics. RT fundamental harmonics can be tuned to a first phonon harmonics of an emitter material, such as TiH<sub>2</sub>. Higher harmonics will be automatically matched, thereby providing for electrons to be sorted from the Fermi distribution tail resulting in higher efficiencies. RT leak currents are extremely small compared to other

types of barriers. For example, the probability of an electron with 0.1 eV energy to penetrate the RT barrier 81 is much less than for an electron with 0.25eV energy. This type of sorting efficiency provides for a high converter efficiency.

### 3. Collector

The collector 16 material must have the properties set forth below to assure proper operation of the converter. The collector 16 must provide thermal and electrical conductivity. Figure 15A illustrates a collector 16 having a substrate 88, which is not electrically conductive, coated with a conductive or doped layer 90 for electrical conductivity. If the collector 16 is used as a substrate for the electron sorting barrier 14, it must be polished to a surface finish that is superior to the barrier 14 thickness. For example, with a barrier 14 thickness of 150-200Å, the surface finish must be better than 50Å over the entire collector 16. Metals meeting a surface finish requirement of <50Å are known in the metals optics industry. Such metals include, but are not limited to, Cu, Mo, W, Al, combinations thereof, or equivalents thereof.

An alternative approach is to utilize optically polished dielectric or semiconductor collectors 16, which have good thermal conductivity and are coated with a conductive or doped material to achieve the requisite electrical conduction. Such materials include, but are not limited to, silicon, gallium arsenide, sapphire, quartz (fused silica), or equivalents thereof. These materials are readily available with a surface finish better than 10Å. Glass has a low thermal conductivity of 1-2 W/(m·K) and is therefore only practical in low power density converters. Refractory single crystals and diamond can be used for more stringent applications.

For embodiments utilizing a high phonon energy material as the emitter 12, the collector 16 must not have a high energy component in its phonon spectrum. Moreover, the collector 16 material must have an atomic mass sufficient to have a spectrum cutoff below  $kT$ , since the phonon frequency normally decreases with the mass of a metal atom. The list of metals meeting this criteria are set forth in Landolt-Börnstein, *Numerical Data and Functional Relationships in Science and Technology, Group III: Crystal and Solid State Physics*, (1981) Vol. 13a *Metals: Phonons and Electron States. Fermi Surfaces*, pp. 7-180, and Khotkevich et al., *Atlas of Point contact Spectra of Electron-*

*Phonon Interactions in Metals*, (1995), the contents of which are specifically incorporated herein. Examples of such metals include, but are not limited to, Au, Bi, Hf, Pb, Pt, W, Zr, Ta, and Sn.

The thermal expansion coefficient of the collector 16 material preferably should be matched to that of the barrier 14 material to prevent coating peel-off during operation of the converter under thermal cycling. In addition, the collector 16 material must have sufficient mechanical integrity to withstand operation temperatures.

When the materials of the barrier 14 and the collector 16 are not selected so as to prevent the leak back of electrons through the barrier 14, an electrically conductive, barrier matching material 92 must be disposed between the collector 16 and the barrier 14 (See Figure 15B). The selection rule for the barrier matching material 92 with an electron work function  $\phi_c$ , an emitter 12 material with an electron work function  $\phi_e$ , and a barrier 14 material with an electron work function  $\phi_b$ , is:  $\phi_c > \phi_b \geq \phi_e$ . The actual  $\Delta\phi$  depends on the operating temperature and application.

The electron energy in an emitter 12, barrier 14, and collector 16 will be positioned according to their electron work function, when measuring the electron energy from the vacuum energy level as a reference point. When the work function of the collector 16 material is too low, the collector 16 functions as an additional barrier for emitted electrons and, therefore, should be avoided. Metals such as Pt or Ir have a very high work function and are preferred. However, they may not be necessary when the emitter material has a low electron work function.

#### 4. Examples

##### 4(a). Converter with Dielectric Barrier

A converter was assembled using an emitter comprising tantalum-hydride powder 17 housed in a honeycomb structure 18 (See Figure 3). The converter was assembled on a rigid microscope frame with a microscopic linear positioning stage providing for a  $\pm 0.5$  micron spacing regulation. A cartridge heater (Omega, 100W) was fed with a regulated DC power supply, and thermal contact to the tantalum-hydride powder was provided by a polished copper rod. Both the heater and the rod were enclosed in Macor insulation and spring loaded to the microscope stand. A water cooled heat sink made of

copper was mounted on a positioning stage with an additional laser mirror mount, which provided for 3D alignment of the contacting planes. Cooling water was supplied from a large tank at room temperature by means of a peristaltic pump at  $\pm 0.5^\circ\text{C}$  stability over a one-hour interval. The temperature of the copper rods was measured with two platinum  
5     RTDs connected to a Keithly 2001 multimeter for data acquisition ( $\pm 0.02^\circ\text{C}$  accuracy). A stainless steel envelope of each RTD was also used as electric leads to make a connecting circuit between the emitter and collector. The voltage in the external circuit was measured with a Hewlett Packard model HP34420A nanovoltmeter ( $R_n = 10$  Gigaohm).

10     A sample I-V curve was measured with a Kepco ABC 25-1DM external power supply and a Keithly 2001 as an ammeter. A resistor bank (1% accuracy) was connected in parallel with the circuit, allowing up to 0.5 Gohm loads without interfering with the nanovoltmeter. The I-V curve was defined by voltage-load measurements. The emitter  
15     powders 17 included either TaH or  $\text{TiH}_2$  particles, ball-milled from an initial 10-20 micron size to 0.2 - 0.3 micron average particle size. The emitter was formed either by tapping the powder 17 into a low thermal conductivity honeycomb structure 18 glued to a copper plate, or by drying a powder suspension in alcohol on the copper plate. The honeycomb structure 18 utilized in this prototype was procured from Goodfellow Corporation, located in Berwyn Pennsylvania. The part number of the honeycomb  
20     structure is AR312610 having the following specifications: 5 mm thickness, 0.05 mm cell wall, and 3 mm cell size.

A variety of collector substrates were tested, including metallized, optically polished sapphire, optically polished Kovar and molybdenum, and metallized optical glass. A barrier matching material 92 having a thickness of 200-500Å was deposited on  
25     a substrate 90, for example, Ta for a TaH emitter. Dielectric layers of  $\text{Al}_2\text{O}_3$  were deposited by PVD (physical vapor deposition, magnetron sputtering), or CVD (chemical vapor deposition). The impurity, or defect, concentration on the collector samples, deposited by both means, was not meticulously controlled. The minimum barrier thickness achieved, that was not electrically shorted over a  $1\text{ cm}^2$  area, was approximately  
30     250Å. In some samples the barrier was not shorted at room temperature, but failed at 35-40°C. The highest observed voltage was 0.22V using dielectric barriers at a temperature

difference of 35°C between the emitter and collector. The highest observed current was about 2μA. Some of the samples had an S-type current-voltage curve, which is typical for tunneling diodes (See Figure 16). In Figure 16, the temperature of the emitter was approximately 31.96°C, and the temperature differential between the emitter and the collector was approximately 11.06°C. The S-curve 94 is not smooth, suggesting the existence of a localized conduction band in an amorphous dielectric. Some samples had I-V curves 96 and 98 resembling the initial portion of a tunneling S-curve (See Figure 17). For I-V curve 96, the temperature of the emitter was approximately 22.5°C, and the temperature differential between the emitter and the collector was approximately 3.1°C. For I-V curve 98, the temperature of the emitter was approximately 24.5°C, and the temperature differential between the emitter and the collector was approximately 5.4°C. In Figure 18, line 100 indicates the voltage dependence on the temperature gradient, which was basically linear for most of the samples. The linear  $V(T)$  line 100 indicates a phonon mechanism, which should depend linearly on the heat flow through the sample. The heat flow is a linear function of the temperature difference, while the electron distribution is an exponential function with temperature.

These tests provided an initial proof-of-concept for a converter with a voltage output of up to 10-15 mV/K, which is significantly higher than any known thermoelectric device. The current density for the converter utilizing an Al<sub>2</sub>O<sub>3</sub> barrier was low, which is expected for relatively thick barriers and the absence of conduction band control. However, the conduction band can be engineered. Continuous layers of Al<sub>2</sub>O<sub>3</sub> are taught in the literature, with some as low as 20Å, and a factor of 10<sup>6</sup> times gain on current can be achieved.

#### **4(b). Converter with Semiconductor Barrier**

A converter was made utilizing PbTe coatings as a semiconductor barrier, deposited by magnetron sputtering. The magnetron sputtering target was 99.99% pure p-type PbTe doped with Al to 0.3 - 0.5 atomic %. PbTe has a high electron work function (4.8 - 5.1 eV) that creates challenges in forming a barrier that will prevent a backflow of electrons. Only a limited number of metals have a higher electron work function, such as Pt and Au. A polished glass substrate was coated with 3000Å layer of

Ta for electrical conductivity, with 500Å of gold barrier matching, and 350Å of PbTe as a barrier material. The Schottky barrier height in this case was not known.

At PVD temperatures of 100-200°C, PbTe usually forms a crystalline coating. The deposition temperature of the sample in this case was 30-100°C; therefore, an amorphous coating is not excluded.

Test results are shown below in Table 2, wherein a TaH powder emitter was utilized with a cross-sectional area of 17mm<sup>2</sup>. The emitter temperature was 26.9°C and the collector temperature was 22.0°C.

TABLE 2

Resistive Load (ohms)	Output Voltage (mV)
10 <sup>6</sup>	5.2
10 <sup>4</sup>	2.7
10 <sup>3</sup>	2.4
500	2.3
100	2.2
10	0.020

The results show that the "over the barrier" current was apparently not achieved, since the voltage spread is too small, e.g., 5.2mV when compared to an expected range of more than 100mV. This means that the actual potential barrier in this case was more than, or close to, 1eV. The conductivity appears to be similar to a phonon-assisted impurity conduction band conductivity in a dielectric. Nevertheless, the recalculated efficiency of this device was 5.7% of an ideal Carnot cycle without accounting for the thermal conductivity of air. The efficiency is 6.6% when taking into account the thermal conductivity of air at temperature of 300K and a temperature differential of 4.9K. The measurement errors were insignificant with 10<sup>-3</sup>% on the voltage side, 1% on the resistance (current) side, and 0.02°C on the temperature side. The temperature drift during the test was less than 0.2°C.

#### 4(c). Converter with Semiconductor Barrier

A converter, similar in construction to the converter constructed in Section 4(b) above, was constructed from the same PbTe sputtering target (0.3-0.5 atomic % doping with Al). The main difference between the present converter and that in Section 4(b) was the collector substrate, which was polished to 50Å RMS surface finish aluminum (15 x 12 x 3mm<sup>3</sup>). The Al was coated with 3000Å of Ta and 300Å of Pt. The PbTe layer on top of the Pt layer was 240Å. Also, the emitter comprised TiH<sub>2</sub> microspheres.

The test was performed with an emitter temperature of 31±0.5°C, and a temperature difference between the emitter and collector was 7.5±0.5°C. The resulting I-V curve 102 obtained by varying the load resistor is shown in Figure 19.

The voltage spread was sufficient to resemble over-the-barrier current transport, unlike the I-V curve produced in Section 4(b). Efficiency estimations cannot be made because the Al substrate has a high thermal conductivity. However, the output of the present converter is higher than that produced in Section 4(b).

#### 5. Refrigeration Embodiments

The main components of a thermionic converter 104 for providing refrigeration (see Figure 20) are essentially the same as those of a thermionic converter 10 for converting heat to electricity, as set forth above. The essential difference is that carrier transport is assisted by an external electric field,  $E_{Ext}$ , and the emitter 12 is connected to a thermal load. The emitter 12 is thermally insulated by means of an insulating material 106. Rather than a heated emitter 12, as is the case in the heat to electricity embodiment, a thermal load is cooled by heat flow,  $Q_{Load}$ , to the emitter 12 in the thermionic converter 104 illustrated in Figure 20. The back surface of the collector 16 acts as a heat exchanger, and heat flow  $Q_{Exchange}$  dissipates the heat from hot electrons. One skilled in the art of heat exchangers recognizes there are many means for accomplishing heat exchange including, but not limited to, air and liquid cooling, or equivalents thereof.

Barrier configurations that provide for a large thermal separation between the emitter 12 and collector 16 are set forth above.

It is important to note that phonon-assisted electron transport is less important in the refrigeration embodiment than in the heat-to-electricity embodiments, because the

refrigeration mode depends primarily on the operating voltage. For example, there cannot be more than a 0.3eV gain from phonons at significant currents. The operating voltage can be obtained from an external voltage source,  $E_{ext}$ .

Figure 21 illustrates a thermionic converter 108 for providing refrigeration, which utilizes a barrier 14 in the form of point contacts. The barrier 14 may comprise, for example, spherical semiconductor particles similar to the embodiment illustrated in Figure 1.

The barrier 14 illustrated in Figure 22 comprises particles having a thin semiconductor layer 114 that allows ballistic carrier transport, a conductive or doped layer 112 for electrical conductivity and electron work function matching, and a core material 110 (see Figure 22). The core material 110 may be a dielectric, conductive or doped material, semiconductor, or plastic, if it is sufficiently hard and has suitable operating temperatures and thermal expansion coefficients. In this embodiment, one side of the particle will function as an emitter and the other side as a collector. It is also important to note that the conductive or doped layer 112 must have an electron work function value between that of the emitter 12 and collector 16.

## 6. Applications

Since energy conversion is the basis of modern civilization, an efficient energy converter has numerous applications, such as existing utility power plants, solar power plants, residential electricity supplies, residential/solar electricity supply, automotive, maritime, solar/maritime, portable electronics, environmental heat pump, refrigeration (cooling, air conditioning, etc.), aerospace, and so forth.

Power plants have a tremendous amount of waste heat with a potential of 300°C and lower. Converting the waste heat at 20-40% of Carnot efficiency will give an additional 10-20% overall plant efficiency with equivalent savings on fuel.

The proliferation of low-cost converters will lower the capital costs of solar concentrator power plants with a higher efficiency than current steam/electricity cycles. Lower operating temperatures will also lower maintenance costs.

Residential electric supplies based on direct heat to electrical energy conversion is ideal for remote areas, where it is difficult or inconvenient to install power lines. The

heat source may either be in the form of fossil fuel or solar concentrators. Solar concentrators can also be in the form of solar heated water pools, utilizing day/night temperature differences. A few hundred cubic meters of water with a hundred square meters of surface and cover could provide the electricity supply for a house in areas with a temperature differential of about 10°C.

A thermionic converter in combination with a conventional engine driving an electric generator and an electric motor would substantially increase mileage.

Direct energy conversion has tremendous application in electric cars. One application involves using thermionic devices with operating temperatures up to about 150 to 200°C as overall efficiency boosters. Another application is an automobile with an electric drive and a conventional engine coupled with an electric generator having a converter array as an intermediate radiator.

Automotive and propulsion applications are also applicable to maritime applications. In addition, solar concentrators may be used in a sail-type fashion. A combination of light and inexpensive plastic Fresnel lenses with thermionic converters may be incorporated into modern rigid wing-type sails, providing for the use of wind and sun energy to propel a boat with about 100-200 W/m<sup>2</sup> of the sail solar component.

Since the converter can utilize very small temperature gradients in a self-sustaining mode, a temperature gradient between the heat sinks will be created with asymmetric heat exchange on the surface (e.g. one heat sink can be thermally insulated). Also, the system will run until something malfunctions, cooling the environment and producing electricity. In summary, the method and apparatus disclosed herein is a significant improvement from the present state of the art of thermionic energy conversion.

The invention may be embodied in other specific forms without departing from its spirit or essential characteristics. The described embodiments are to be considered in all respects only as illustrative and not restrictive. The scope of the invention is, therefore, indicated by the appended claims rather than by the foregoing description. All changes which come within the meaning and range of equivalency of the claims are to be embraced within their scope.

What is claimed and desired to be secured by Letters Patent is:

## CLAIMS

1. A solid-state thermionic converter comprising:  
an electrically and thermally conductive electron emitter;  
5 an electrically and thermally conductive electron collector for receiving  
electrons from the emitter;  
a barrier disposed between said emitter and collector for filtering high  
energy electrons transferred from the emitter to the collector;  
one or more electrically and thermally conductive fractional surface  
10 contacts integral to said emitter, barrier, or collector and disposed between and in  
intimate contact with the emitter and barrier, or the barrier and collector, or a combination  
thereof;  
a thermally and electrically nonconductive space adjacent to the fractional  
surface contacts and the emitter and barrier, or the barrier and collector, or a combination  
15 thereof; and  
an electric load connected to said emitter and collector.
2. An apparatus according to Claim 1, wherein said emitter comprises a  
metal, a metal, a semiconductor material, or doped semiconductor material.
- 20 3. An apparatus according to Claim 1, wherein said emitter comprises an  
electrically and thermally conductive layer on a substrate.
4. An apparatus according to Claim 1, wherein said emitter comprises a  
25 material having a high phonon energy spectra.
5. An apparatus according to Claim 4, wherein said material comprises  $\text{TiH}_x$ ,  
 $\text{VH}_x$ ,  $\text{ZrH}_x$ ,  $\text{NbH}_x$ ,  $\text{TaH}_x$ ,  $\text{ScH}_x$ ,  $\text{YH}_x$ ,  $\text{ThH}_x$ ,  $\text{UH}_x$ , all rare earth hydrides, or combinations  
thereof.

6. An apparatus according to Claim 1, wherein said emitter comprises a substrate of BH, B<sub>4</sub>C, BN (hexagonal), BN (cubic), diamond, or combinations thereof, with a conductive or doped layer disposed between the substrate and the barrier.

5 7. An apparatus according to Claim 6, wherein said conductive or doped layer has a thickness less than the electron mean free path in said conductive or doped layer.

10 8. An apparatus according to Claim 1, wherein said collector comprises a metal, a metal alloy, a semiconductor, or doped semiconductor material.

9. An apparatus according to Claim 1, wherein said collector comprises a electrically and thermally conductive layer on a substrate.

15 10. An apparatus according to Claim 1, further comprising a barrier matching material disposed between the barrier and the collector to prevent leak back of electrons.

20 11. An apparatus according to Claim 1, wherein said barrier comprises Si, n-type Ge, p-type Ge, n-type GaAs, n-type InAs, n-type GaSb, n-type InSb, Sb, n-type PbS, n-type PbSe, p-type Cu<sub>2</sub>O, p-type Se, n-type CDs, DySi<sub>2</sub>, IrSi<sub>3</sub>, Hg<sub>x</sub>Cd<sub>1-x</sub>Te, p-type Ge, amorphous B, LaB<sub>6</sub>, YbB<sub>6</sub>, Pd<sub>2</sub>Si, n-type PbTe, p-type GaAs, -type InP, or combinations thereof.

25 12. An apparatus according to Claim 1, wherein said barrier comprises a resonant tunneling barrier.

30 13. An apparatus according to Claim 12, wherein said resonant tunneling barrier comprises two or more barriers with a spacing between the barriers that provides for electrons to form a standing wave.

14. An apparatus according to Claim 1, wherein said barrier comprises a moveable barrier.

5 15. An apparatus according to Claim 14, wherein said moveable barrier comprises microspheres, microwires, or fixed pillars.

16. An apparatus according to Claim 1, wherein said barrier comprises a dielectric material.

10 17. An apparatus according to Claim 16, wherein said dielectric material comprises amorphous  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$ .

15 18. An apparatus according to Claim 1, wherein said barrier comprises a first conductive or doped layer, an n-type semiconductor layer, a p-type semiconductor layer, and a second conductive or doped layer.

19. An apparatus according to Claim 1, wherein said barrier comprises a first conductive or doped layer, an n-type semiconductor layer, and a second conductive or doped layer.

20 20. An apparatus according to Claim 1, wherein said barrier comprises a first conductive or doped layer, a p-type semiconductor layer, and a second conductive or doped layer.

25 21. An apparatus according to Claim 1, wherein said one or more fractional surface contacts are in the shape of point contacts.

22. An apparatus according to Claim 1, wherein said one or more fractional surface contacts comprise parabolic-shaped contacts, elliptical-shaped contacts, curved-shaped contacts, or combinations thereof.

23. An apparatus according to Claim 1, wherein said one or more fractional surface contacts comprise nanotubes, particles, dendrites, or combinations thereof.

24. An apparatus according to Claim 1, wherein said nonconductive space comprises a vacuum or nonconductive gas.

25. An apparatus according to Claim 1, wherein said emitter is connected to a thermal load and an electric potential, rather than a load, is applied between said emitter and collector, said collector further comprising a back surface acting as a heat exchanger.

26. A method of building a solid-state thermionic converter for converting heat to electricity comprising:

providing an electrically and thermally conductive electron emitter;

providing an electrically and thermally conductive electron collector for receiving electrons from the emitter;

forming a barrier disposed between said emitter and collector for filtering high energy electrons transferred from the emitter to the collector;

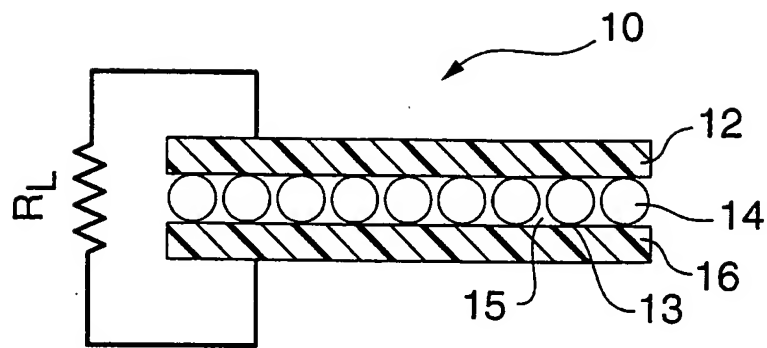
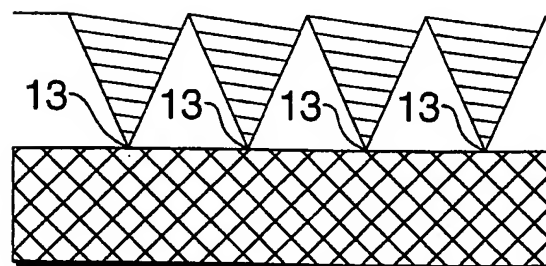
forming one or more electrically and thermally conductive fractional surface contacts integral to said emitter, barrier, or collector and disposed between and in intimate contact with the emitter and barrier, or the barrier and collector, or a combination thereof;

forming a thermally and electrically nonconductive space adjacent to the fractional surface contacts and the emitter and barrier, or the barrier and collector, or a combination thereof; and

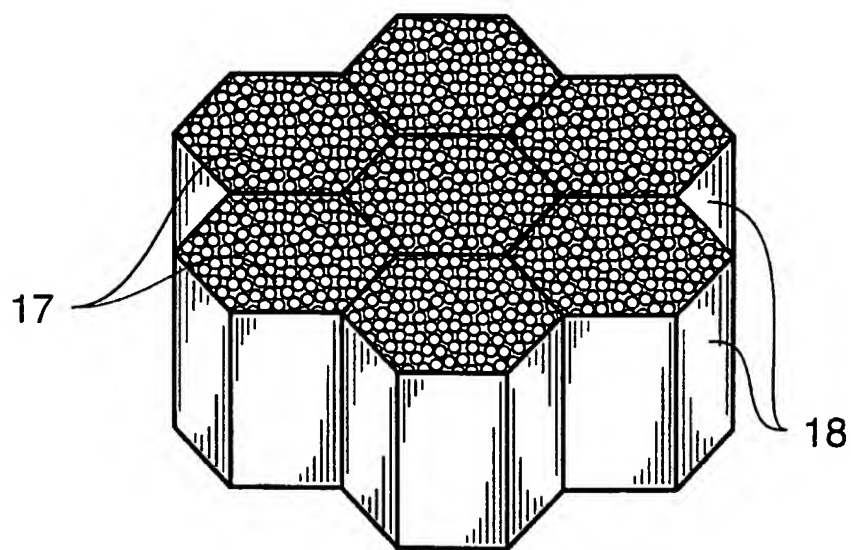
providing an electric load connected to said emitter and collector.

27. A method according to Claim 26, wherein said emitter is connected to a thermal load and an electric potential, rather than a load, is applied between said emitter and collector, said collector further comprising a back surface acting as a heat exchanger.

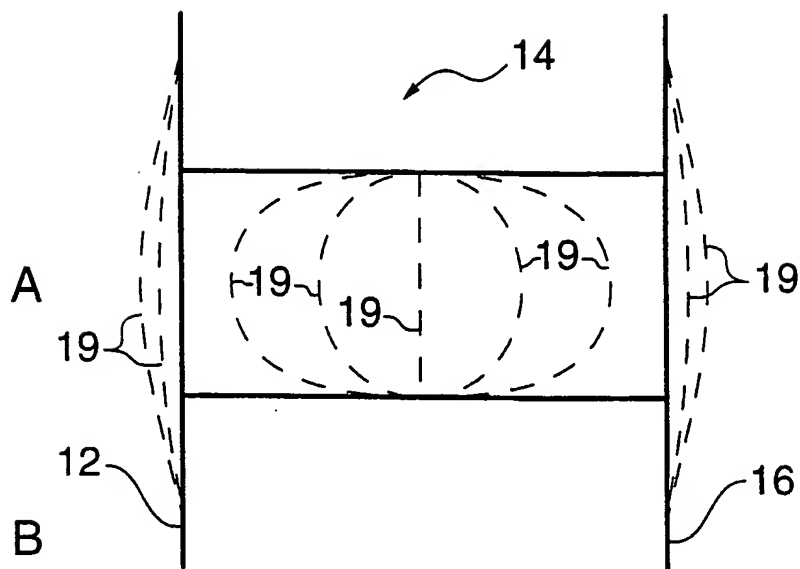
1/13

*FIG. 1**FIG. 2*

2/13

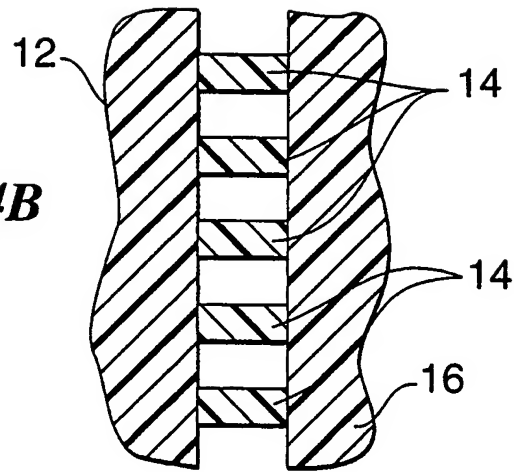
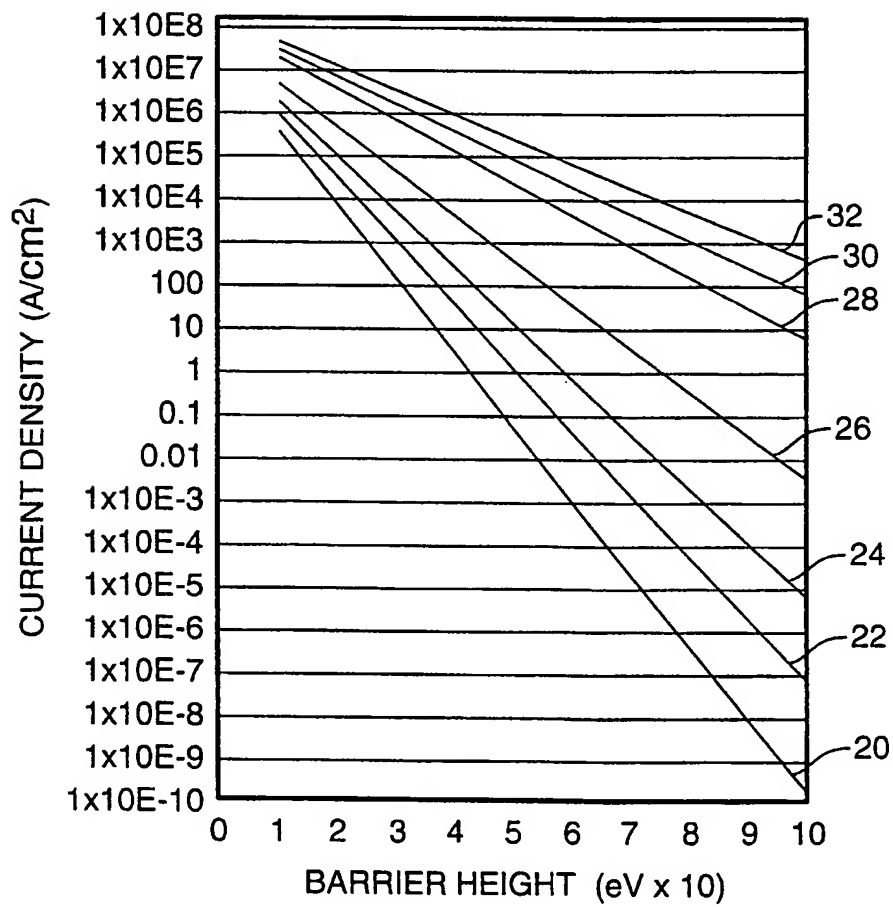


**FIG. 3**

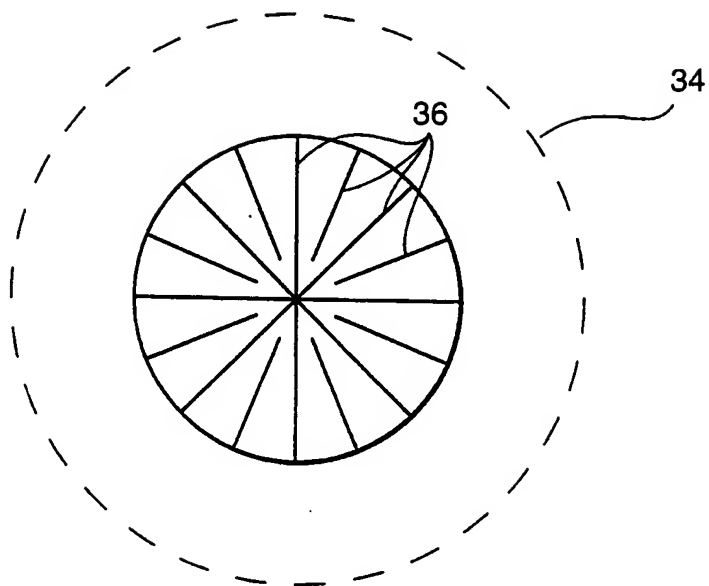


**FIG. 4A**

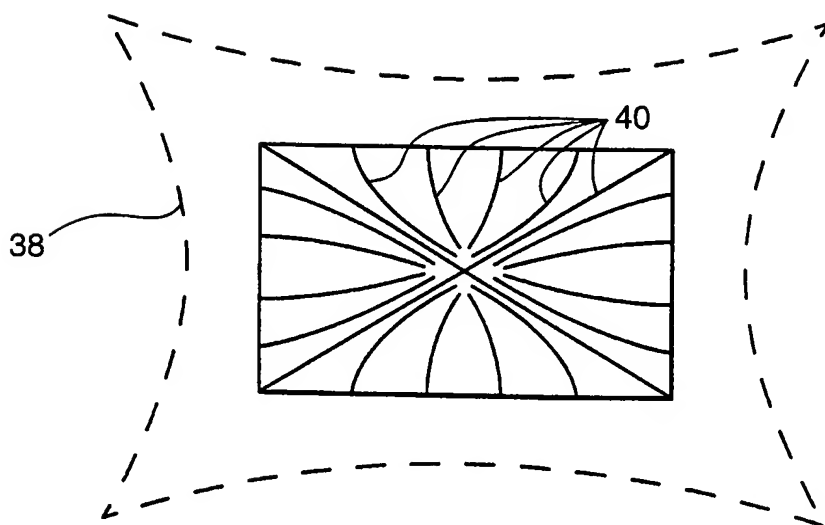
3/13

**FIG. 4B****FIG. 5**

4/13



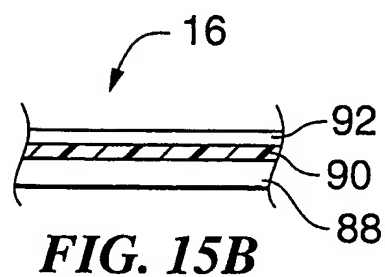
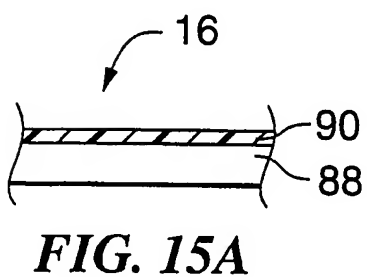
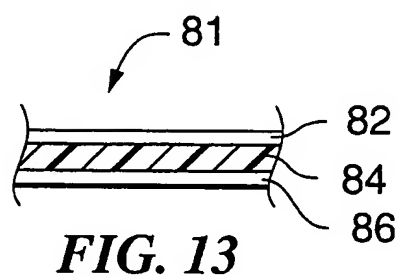
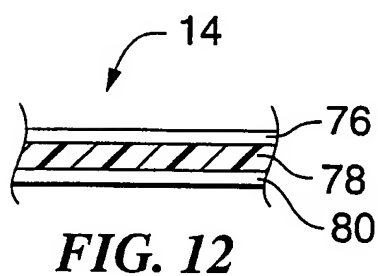
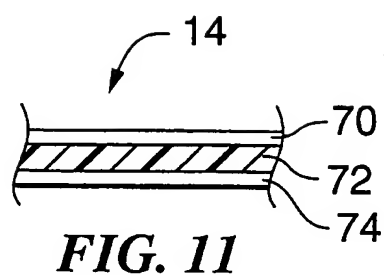
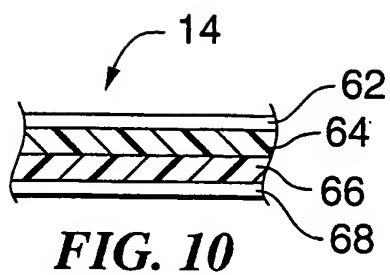
**FIG. 6**



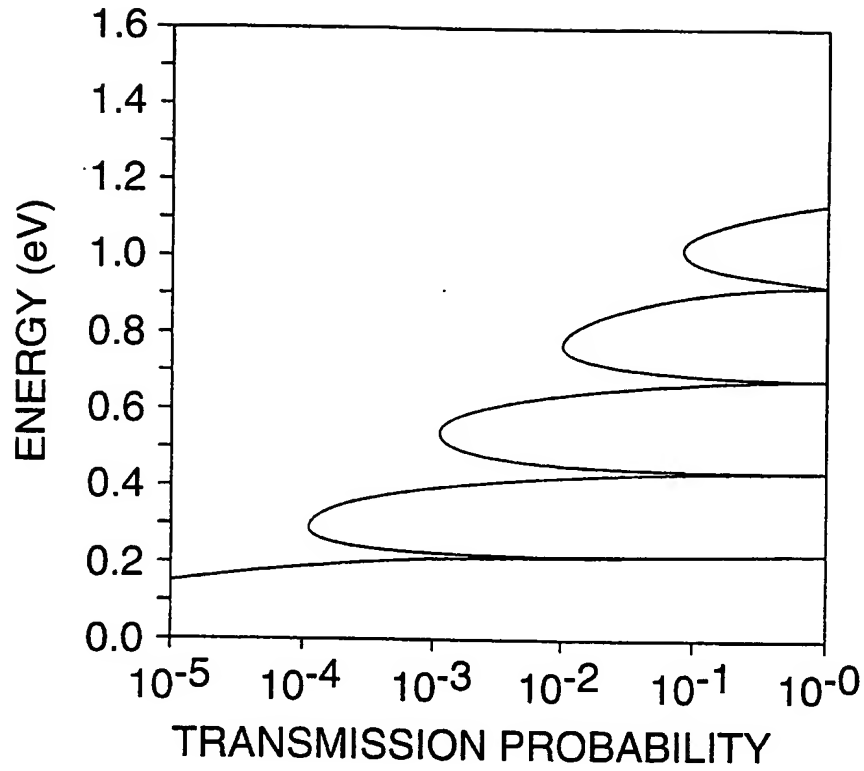
**FIG. 7**



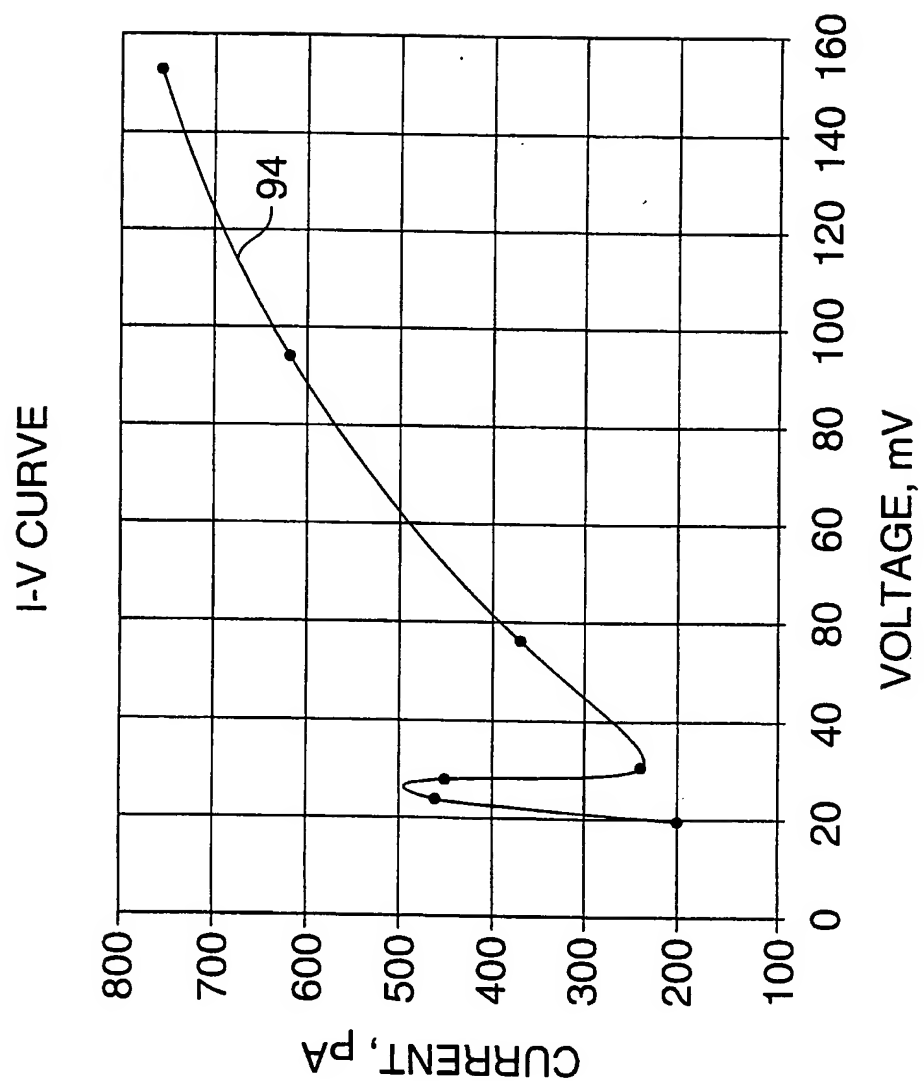
6/13



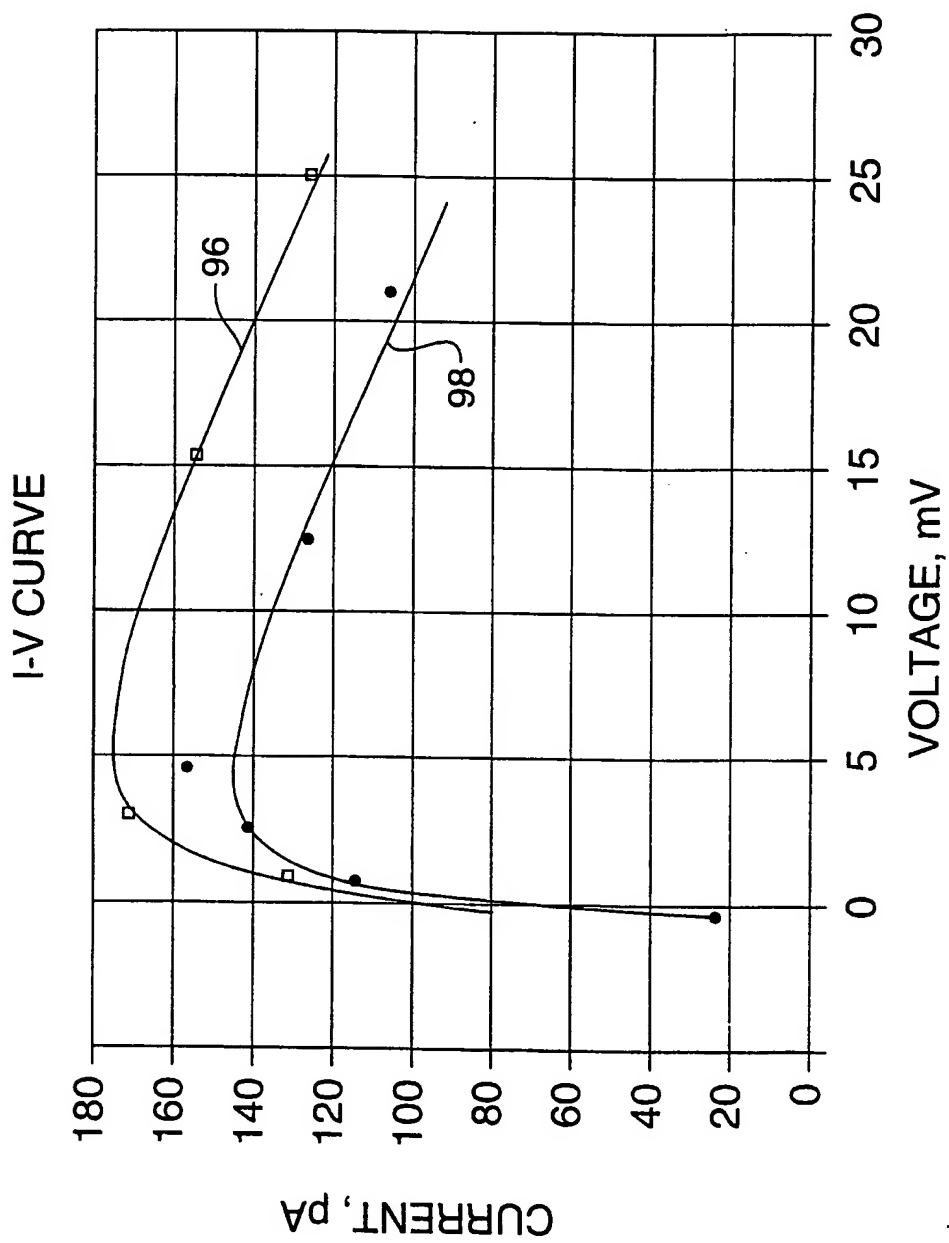
7/13

**FIG. 14**

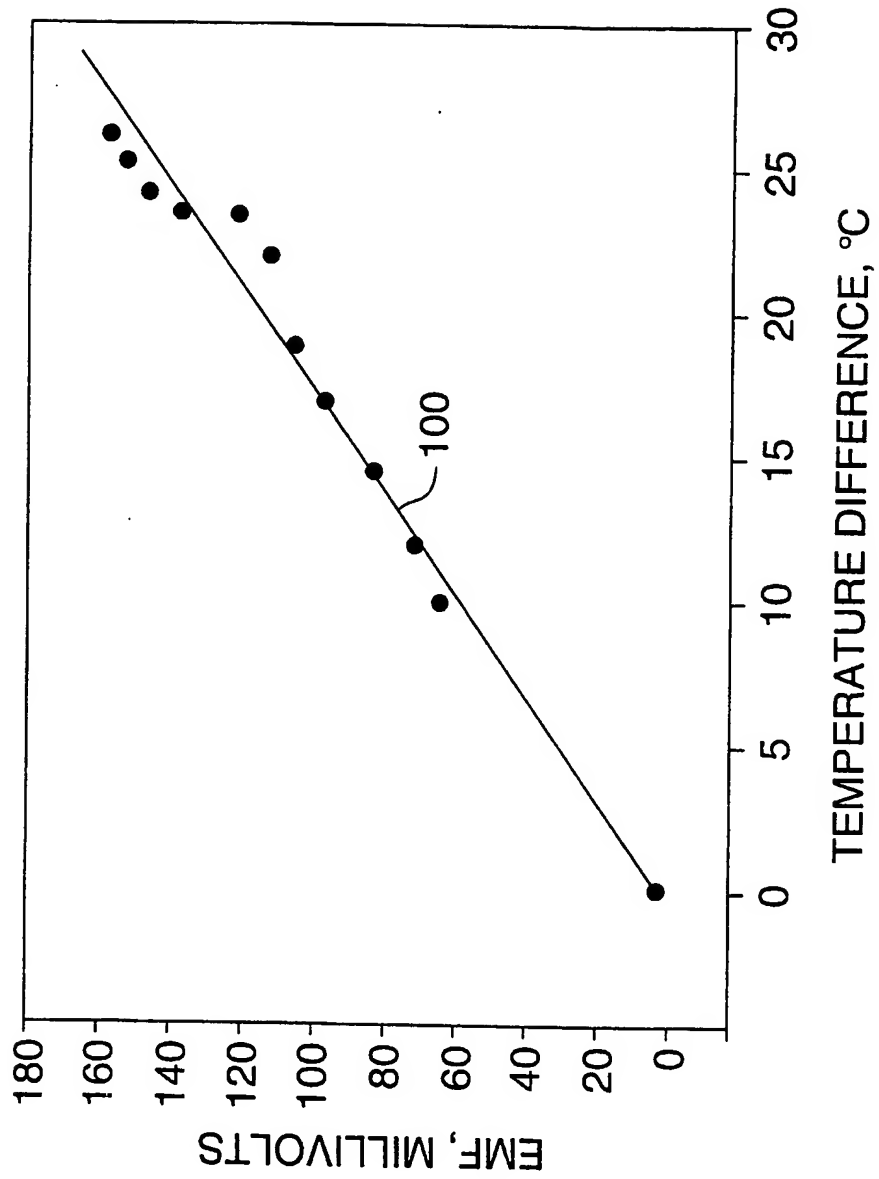
8/13

**FIG. 16**

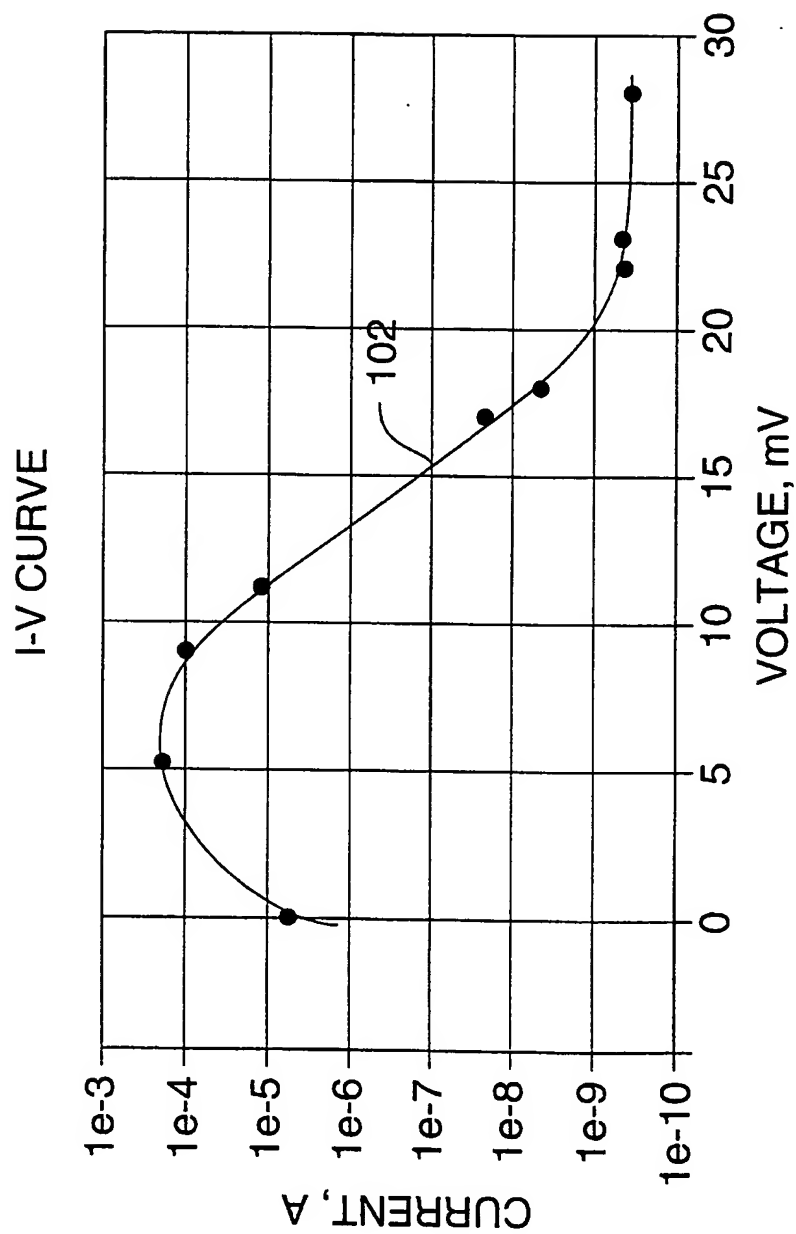
9/13

**FIG. 17**

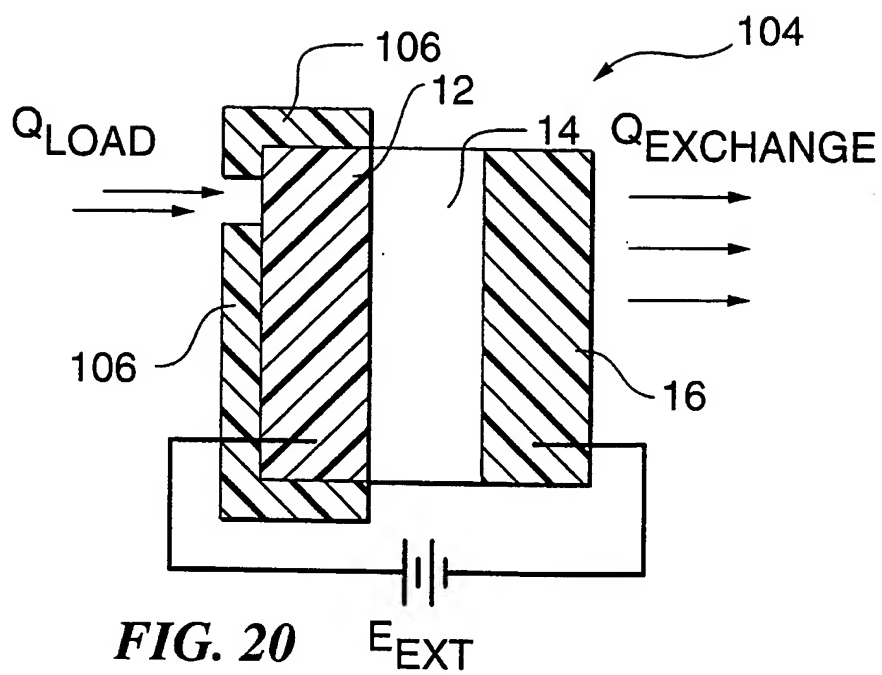
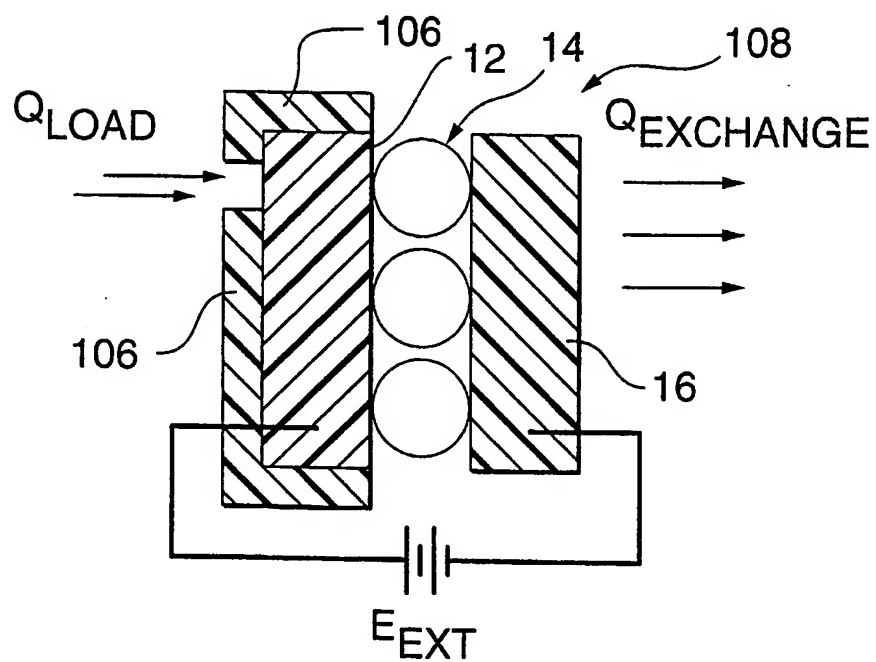
10/13

**FIG. 18**

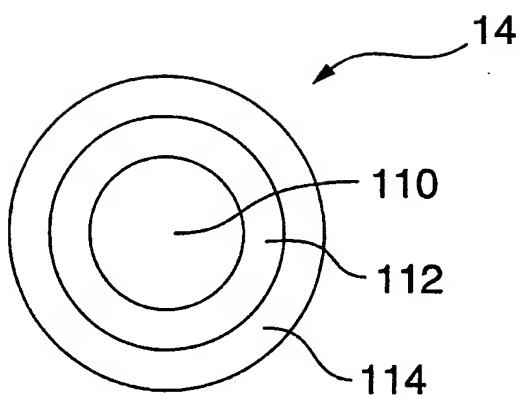
11/13

**FIG. 19**

12/13

**FIG. 20****FIG. 21**

13/13



**FIG. 22**

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/05975**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) :H01L 35/30; H02N 3/00  
 US CL :310/306; 376/321; 322/2R; 136/205  
 According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 310/306; 376/321; 322/2R; 136/205

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
 NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
 NONE

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,E	US 6,037,697 A (BEGG et al) 14 March 2000 (14.03.2000), Figures 1-4.	1-27
Y	US 4,667,126 A (FITZPATRICK) 19 May 1987 (19.05.1987), Figures 1-10.	1-27
Y	US 3,899,696 A (FLETCHER et al) 12 August 1975 (12.08.1975), Figures 1-3.	1-27
Y,E	US 5,994,638 A (EDELSON) 30 November 1999 (30.11.1999), Figures 1-7.	1-27



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

16 AUGUST 2000

Date of mailing of the international search report

30 AUG 2000

Name and mailing address of the ISA/US  
 Commissioner of Patents and Trademarks  
 Box PCT  
 Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

DANG DINH LE

Telephone No. (703) 308-1782 *Heese Pustan*

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**